Supporting Information

Mixed-Ligands Strategy Regulates Thorium-based MOFs

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S1. General Methods

Caution! The thorium nitrate ($Th(NO_3)_4 \cdot 6H_2O$) is a radioactive and chemically toxic reactant, precautions with suitable care and protection for handling such substances should be followed although it was used in the experiment.

$Th(NO_3)_4 \cdot 6H_2O$ (7.35g, 0.0125 mol) was dissolved in deionized water (25 mL) to give a stock solution of thorium nitrate (0.50 M). H_4TCPP were prepared by literature method[1]. H_2bpdc and H_2bpydc were purchased from Aladdin Chemistry Co. 2-chloroethyl ethyl sulfide (CEES) and epoxy styrene were purchased from Sigma Aldrich.

Synthesis of Single Crystal of **Th-IHEP-5**. $Th(NO_3)_4$ (0.50 M, 0.06 mL), H_4TCPP (15.9 mg, 0.02 mmol), H_2bpydc (2.44 mg, 0.01 mmol), DMF (4.0 mL), and concentrated nitric acid (0.4 mL) was loaded into a 10 mL autoclave. The autoclave was sealed and heated to 150 ℃ in an oven for 2 days, then cooled to room temperature naturally. Brown polyhedral columnar crystals of compound **Th-IHEP-5** were produced.

Synthesis of Single Crystal of **Th-IHEP-6**. $Th(NO_3)_4$ (0.50 M, 0.06 mL), H_4TCPP (15.9 mg, 0.02 mmol), H_2bpdc (2.42 mg, 0.01 mmol), DMF (4.0 mL), and concentrated nitric acid (0.4 mL) was loaded into a 10 mL autoclave. The autoclave was sealed and heated to 150 ℃ in an oven for 2 days, then cooled to room temperature naturally. Brown polyhedral columnar crystals of compound **Th-IHEP-6** were produced.

Synthesis of Single Crystal of **NU-905**. Although different from the synthetic methods reported by Peng Li and Farha et al., we also obtained the structure of NU-905 through a single ligand H_4TCPP and thorium nitrate.[2] $Th(NO_3)_4$ (0.50 M, 0.06 mL), H_4TCPP (15.9 mg, 0.02 mmol), DMF (4.0 mL), and concentrated nitric acid (0.4 mL)

was loaded into a 10 mL autoclave. The autoclave was sealed and heated to 150 ℃ in an oven for 2 days, then cooled to room temperature naturally. Brown polyhedral columnar crystals of compound **NU-905** were produced.

S2. Physical Properties

FT-IR measurement was obtained on a Bruker Tensor 27 infrared spectrometer. Sample was diluted with spectroscopic KBr and pressed into a pellet. The measured wavenumber is between 400 and 4000 cm-1. Powder X-ray diffraction (PXRD, Bruker, D8-Advance X-ray Diffractometer) with Cu Kα radiation (λ = 1.5406 Å). Thermogravimetry (TGA, TA Instruments, Q500) was employed in air atmosphere with a heating rate of 5 ºC/min. The N_2 sorption experiments were measured at a liquid nitrogen temperature (-196 ºC) using a micromeritics ASAP 2020 HD88 instrument. The sample was pretreated at 60 ° C for 8 hours after methanol activation. The surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distributions were derived using the nonlocal density functional theory model based N_2 sorption isotherms. ^{1}H NMR spectra were performed on a Bruker Avance III analyzer in Chloroform-d ($CDCl_3$) using TMS as an internal standard.

Single crystal X-ray data were collected on a Bruker APEXII X-ray diffractometer equipped with a CMOS PHOTON 100 detector with a Cu Kα X-ray source (Kα = 1.54178 Å). Data were indexed, integrated and scaled using DENZO and SCALEPACK from the HKL program suite (Otwinowski & Minor, 1997)[3]. The structures were solved by direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-2014) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. The SQUEEZE routine of PLATON was used to remove the diffraction contribution from disordered solvents of compound Th-IHEP-5 and Th-IHEP-6.[4] Pertinent crystal parameters and structure refinement is summarized in Table S1.

Table S1. Crystal data and structure refinement for **Th-IHEP-5** and **Th-IHEP-6**.

Sample	**Th-IHEP-5**	**Th-IHEP-6**
Formula	$C_{114}H_{70}N_{12}O_{24}Th_3$	$C_{116}H_{72}N_{10}O_{24}Th_3$
Formula weight	2687.94	2685.95
Crystal system	monoclinic	monoclinic
space group	*C2/m*	*C2/m*
a (Å)	30.8643(10)	31.969(2)
b (Å)	33.5932(10)	33.2567(19)
c (Å)	16.8652(5)	16.7836(10)
α(deg)	90	90
β(deg)	109.071(1)	106.849(3)
γ(deg)	90	90
V (Å3)	16526.5(9)	17078.04(180)
Z	4	4
ρ_{calc}g/cm^3	1.080	1.045
F (000)	5200	5200
T(K)	170(2)	170(2)
μ/mm^{-1}	9.044	8.748
GOF on F^2	1.063	1.040
R1/wR2 [I>2σ(I)]	0.0351/0.0866	0.0542/0.1329
R1/wR2 (all data)	0.0484/0.0907	0.0711/0.1420

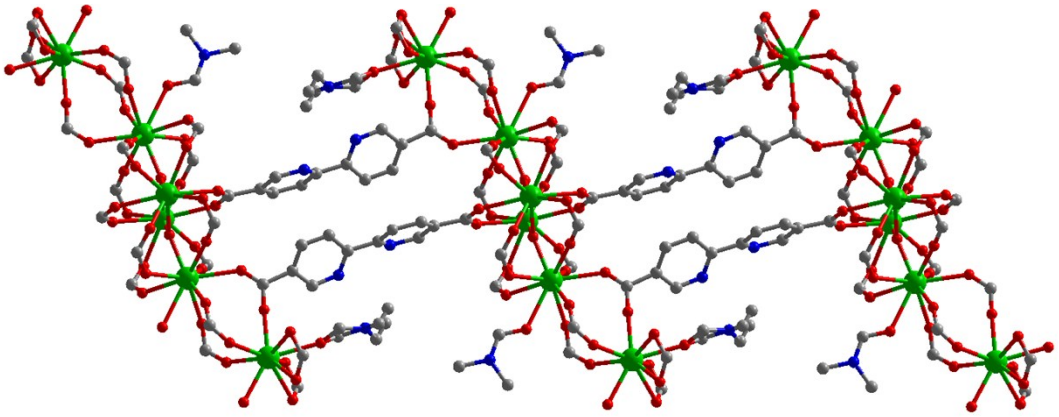

Figure S1. Schematic diagram of coordination mode between H_2bypdc ligands and thorium clusters.

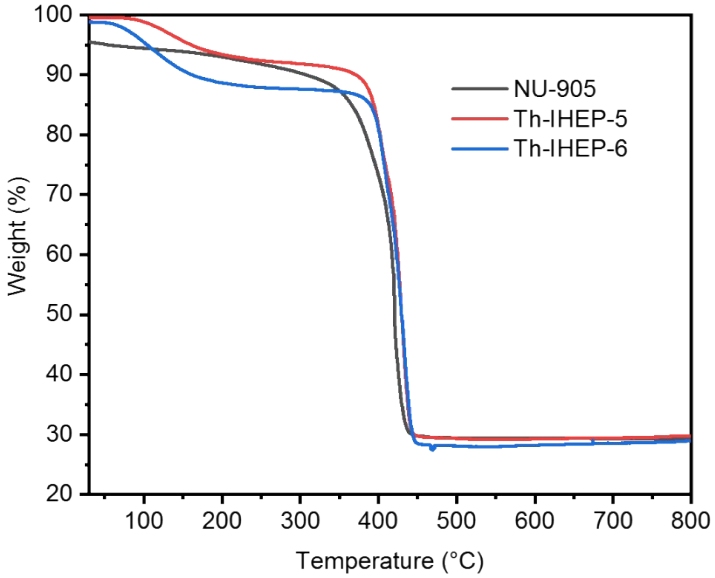

Figure S2. TGA of **Th-IHEP-5**, **Th-IHEP-6 and NU-905** measured under air atmosphere with a heating rate of 5 ℃/min.

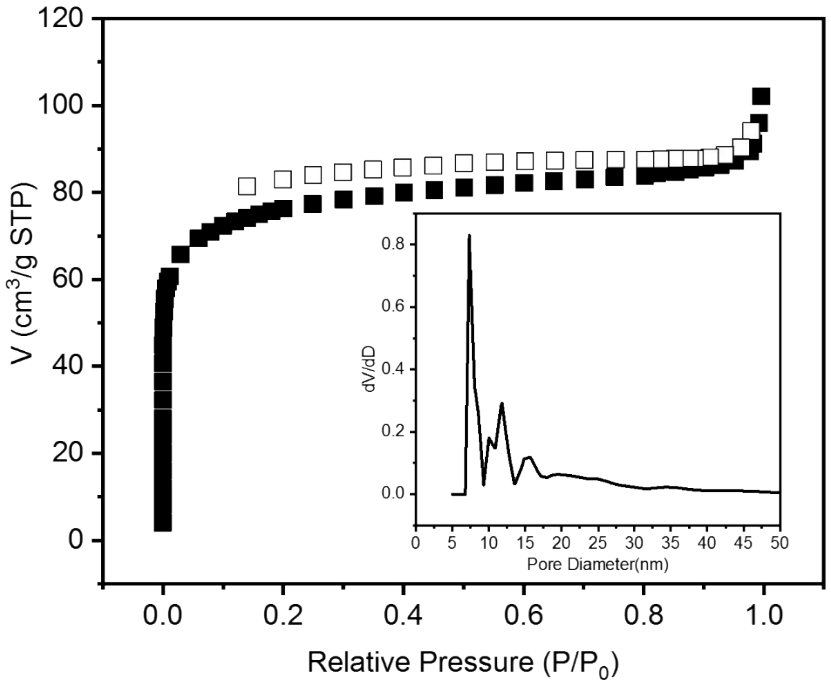

Figure S3. N_2 sorption/desorption isotherm and pore-size distribution of **Th-IHEP-5**.

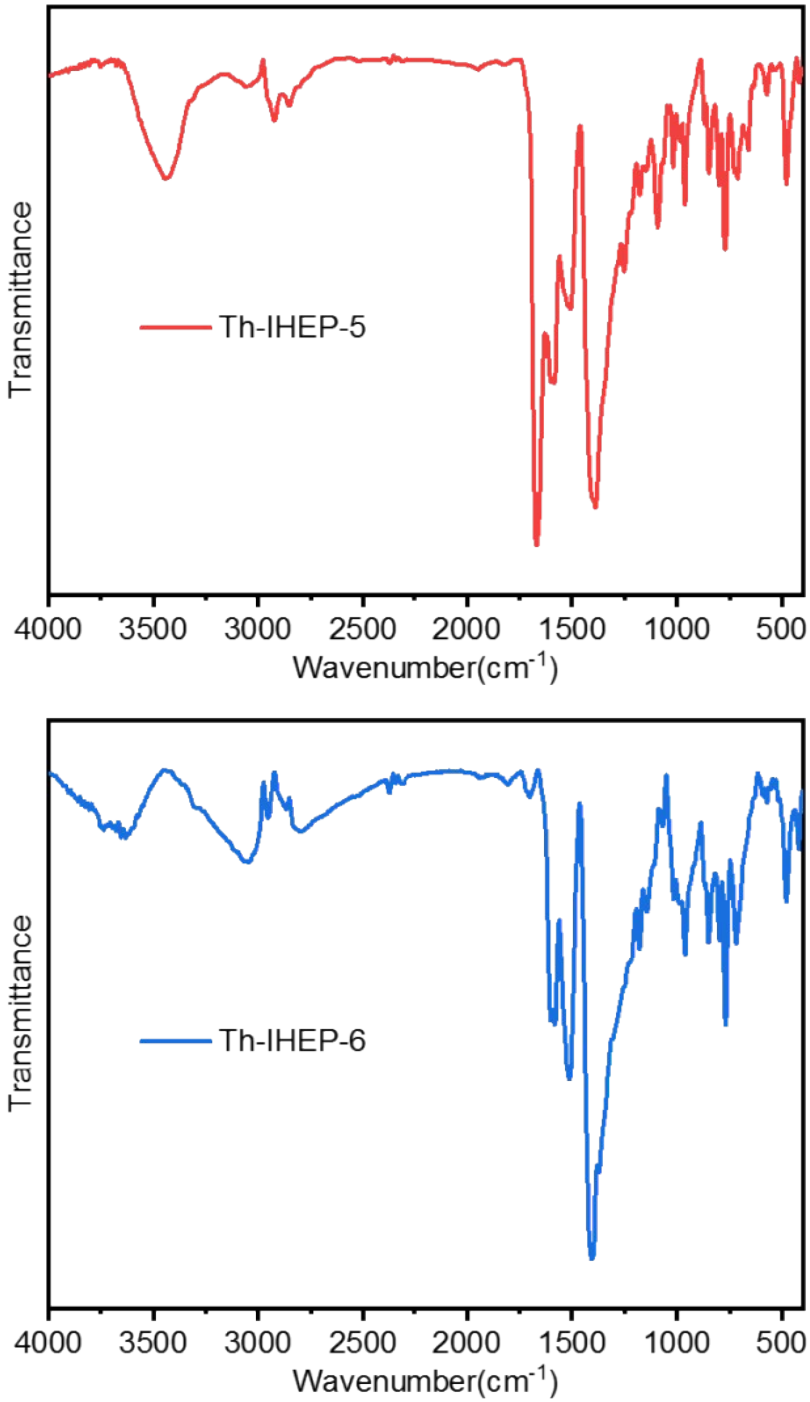

Figure S4. The FT-IR spectrum of compounds **Th-IHEP-5** and **Th-IHEP-6**.

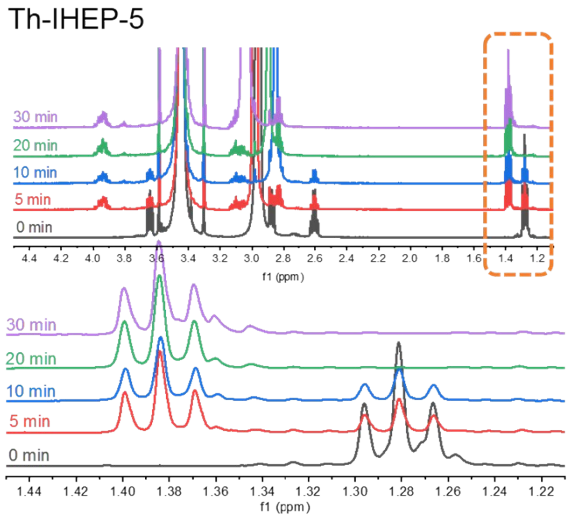

Figure S5. ^{1}H NMR spectrum of kinetic studies of catalysis reaction, using **Th-IHEP-5** as catalyst.

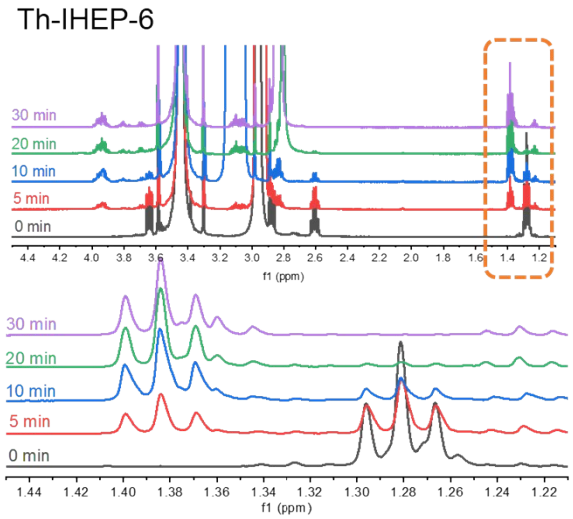

Figure S6. ^{1}H NMR spectrum of kinetic studies of catalysis reaction, using **Th-IHEP-6** as catalyst.

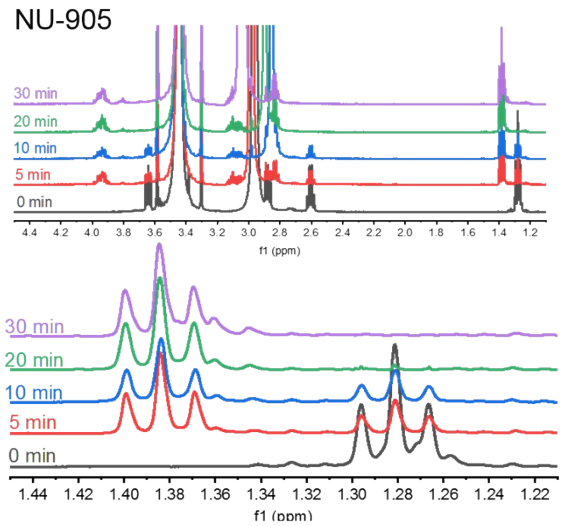

Figure S7. ^{1}H NMR spectrum of kinetic studies of catalysis reaction, using **NU-905** as catalyst.

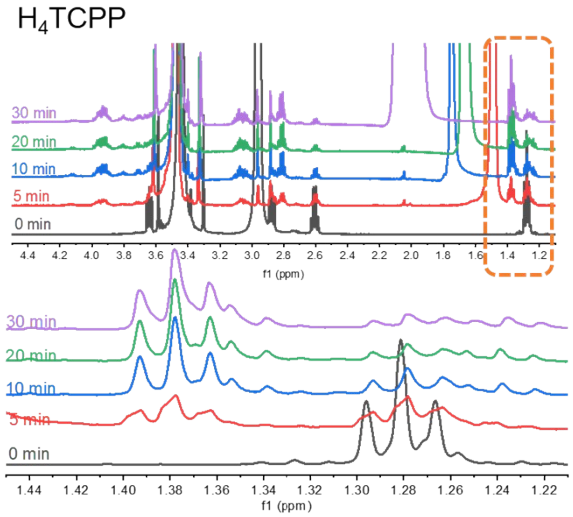

Figure S8. ^{1}H NMR spectrum of kinetic studies of catalysis reaction, using **H_4TCPP** as catalyst.

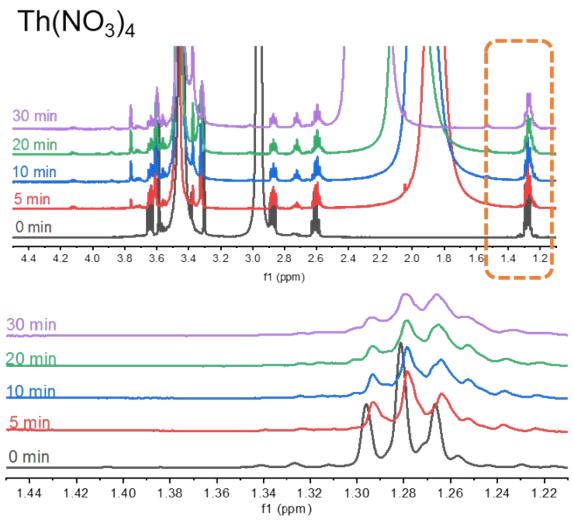

Figure S9. ^{1}H NMR spectrum of kinetic studies of catalysis reaction, using **Th(NO$_3$)$_4$** as catalyst.

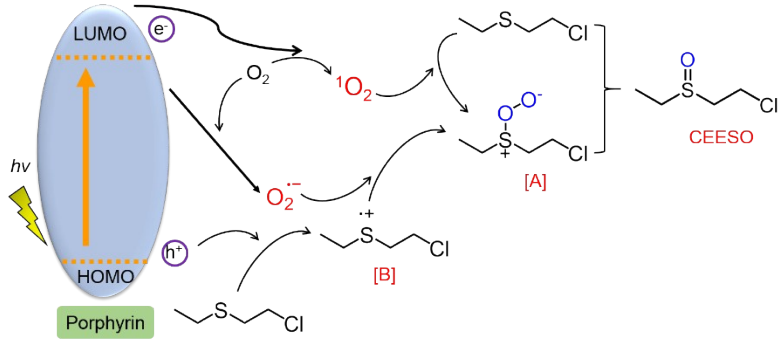

Figure S10. The mechanism diagram of Th-IHEP-5 photocatalytic oxidation of CEES.

Based on existing experimental data and related literature reports[5-7], the possible mechanism of visible light promoting the aerobic oxidation of CEES to CEESO is as follows. Under visible light excitation, Th-IHEP-5 is excited as a photosensitizer and generates photogenerated electron-hole pairs. The light-induced electrons of Th-IHEP-5 can activate O_2 through energy or single-electron transfer processes, producing reactive oxygen species $^{1}O_2$ and $O_2^{\bullet-}$. In one aspect, the reaction between CEES and ^{1}O2 produces the intermediate peroxide [A]. Peroxide [A] further reacts with additional CEES molecules to form the desired product sulfoxide CEESO. On the other hand, the photo-generated holes of Th-IHEP-5 are transferred to CEES, generating sulfur radical cations [B]. The reactive oxygen species $O_2^{\bullet-}$ then reacts with the sulfur radical cation [B], which also produces the intermediate peroxide [A], and finally produces the target product CEESO.

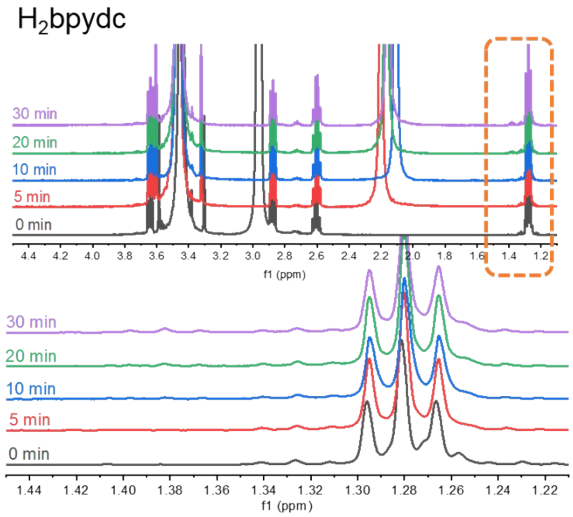

Figure S11. ^{1}H NMR spectrum of kinetic studies of catalysis reaction, using **H_2bpydc** ligand as catalyst.

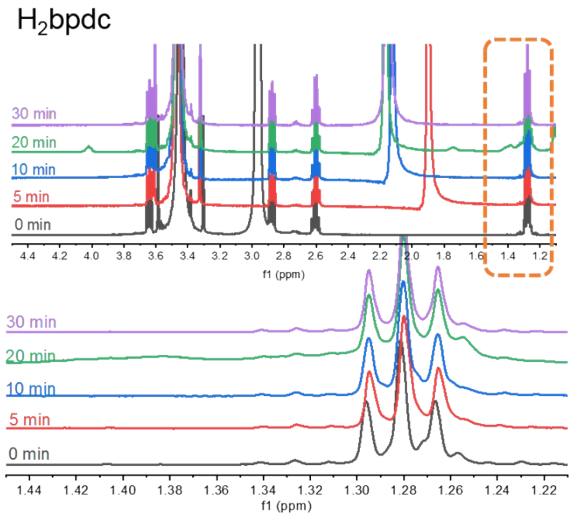

Figure S12. ^{1}H NMR spectrum of kinetic studies of catalysis reaction, using **H_2bpdc** ligand as catalyst.

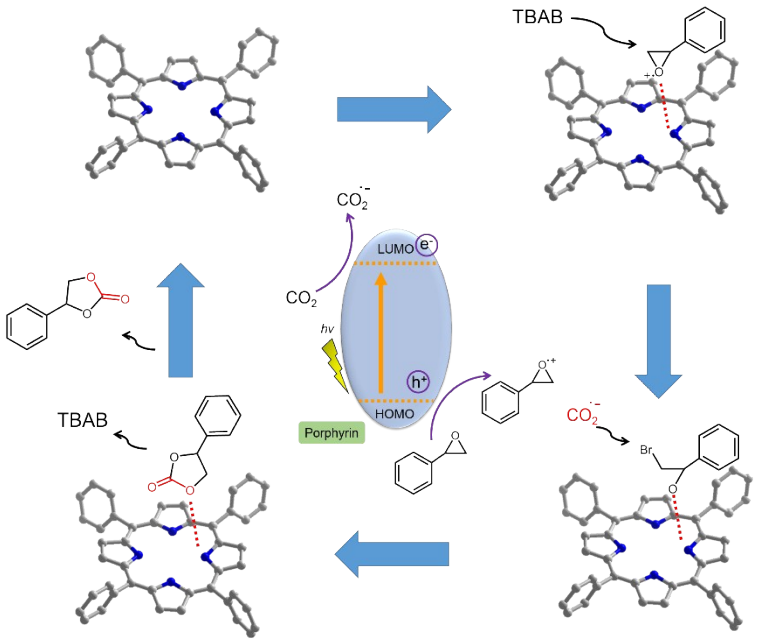

Figure S13. The mechanism diagram of Th-IHEP-5 photocatalytic fixation of CO_2.

According to relevant literature reports,[8-10] the possible mechanism of Th-IHEP-5 photocatalytic fixation of CO_2 is as follows. The process of photoexcitation is similar to that described earlier, CO_2 and epoxy styrene are excited into compounds with free radicals. The epoxides are expected to be activated by hydrogen bonding to the porphyrin ring. Simultaneously, the open-loop reaction occurs by nucleophilic attack of epoxide by Br- to form an oxy ion intermediately. This active intermediate then reacts with CO_2 to form corresponding cyclic carbonates.

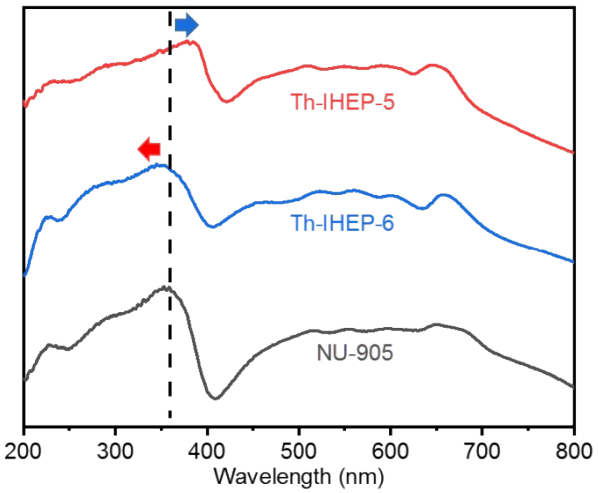

Figure S14. The UV-vis spectrum of compounds **Th-IHEP-5** and **Th-IHEP-6**.

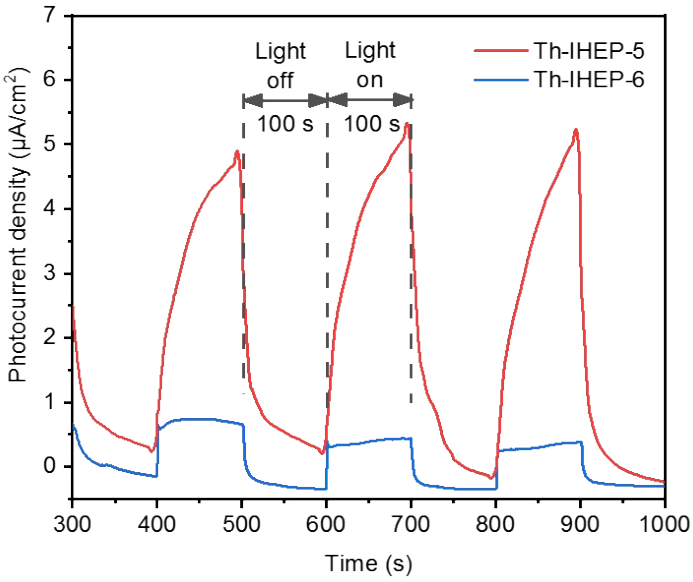

Figure S15. Transient photocurrent responses of **Th-IHEP-5** and **Th-IHEP-6** in 0.1 M Na_2SO_4 solution under 350W xenon light irradiation.

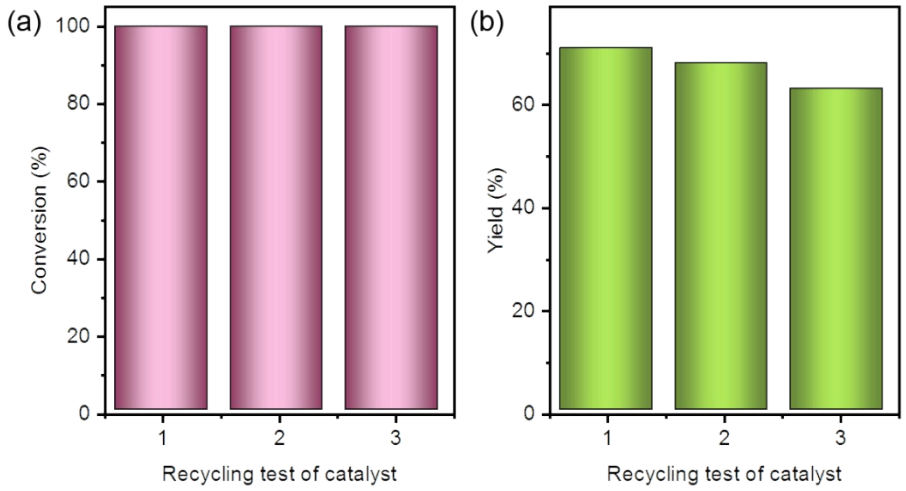

Figure S16. Recycling test of Th-IHEP-5 catalyst, (a) Photocatalytic oxidation CEES, (b) Photocatalytic fixation of CO_2

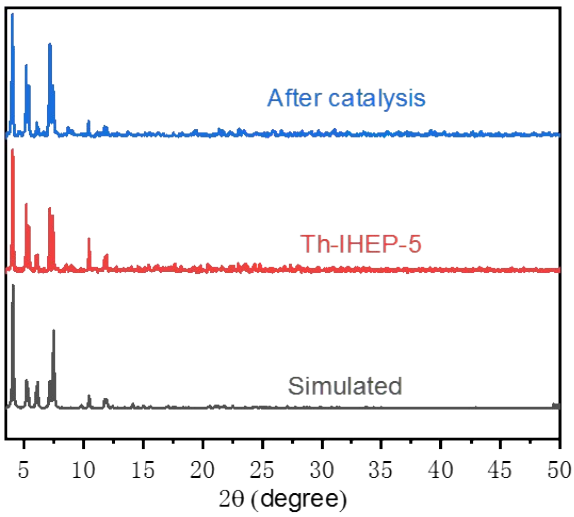

Figure S17. The PXRD patterns for the **Th-IHEP-5** before and after catalysis

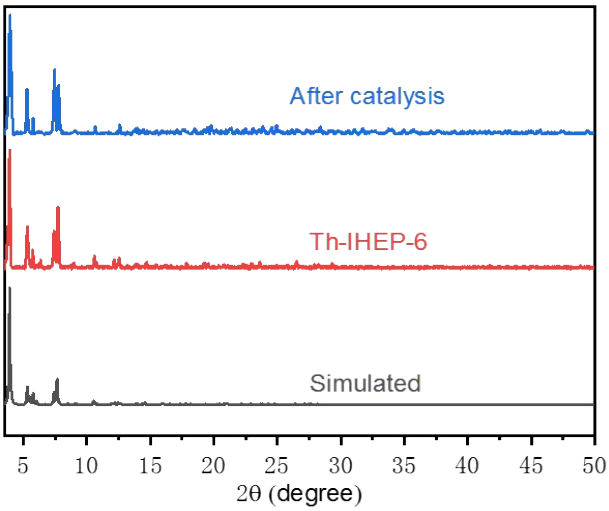

Figure S18. The PXRD patterns for the **Th-IHEP-6** before and after catalysis

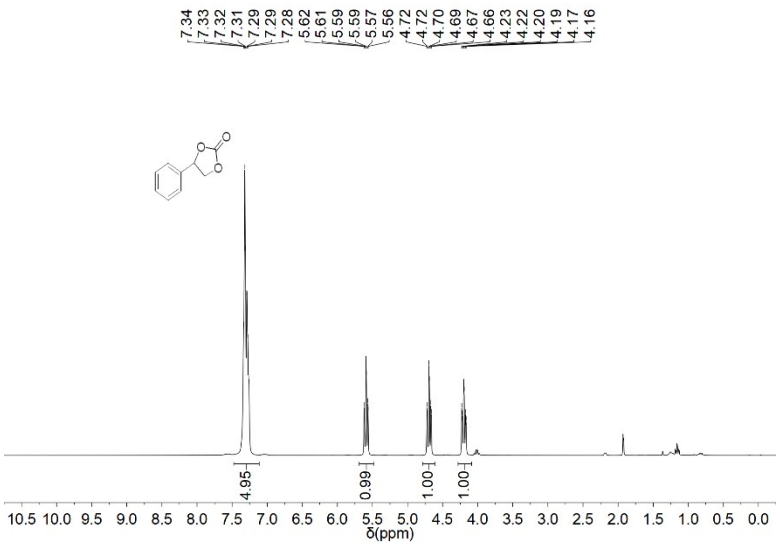

Figure S19. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the product after the CO_2 cycloaddition reaction.

References

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